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Acquisition of Representative Ground Water Quality Samples for Metals

by
Robert W. Puls and Robert M. Powell

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Abstract

R.S. Kerr Environmental Research Laboratory (RSKERL) personnel have evaluated sampling procedures for the collection of representative, accurate, and reproducible ground water quality samples for metals for the past four years. Intensive sampling research at three different field sites has shown that the method by which samples are collected has a greater impact on sample quality, accuracy, and reproducibility than whether the samples are filtered or not. In particular, sample collection practices that induce artificially high levels of turbidity have been shown to have the greatest negative impacts on sample quality. Results indicated the ineffectiveness of bailers for collection of representative metal samples. Inconsistent operator usage together with excessive purging generally resulted in excessive turbidity (>100 NTUs) and large differences in filtered and unfiltered metal samples. The use of low flow rate purging and sampling consistently produced filtered and unfiltered samples that showed no significant differences in concentrations. Turbidity levels were generally less than 5 NTUs, even in fine-textured glacial till. We recommend the use of low flow rates, during both purging and sampling, placement of the sampling intake at the desired sampling point, minimal disturbance of the stagnant water column above the screened interval, monitoring of water quality indicators during purging, minimization of atmospheric contact with samples, and collection of unfiltered samples for metal analyses to estimate total contaminant loading in the system. While additional time is spent due to use of low flow rates, this is compensated for by eliminating the need for filtration, decreased volume of contaminated purge water, and less resampling to address inconsistent data results.

Introduction

Numerous articles, reports, handbooks, and guidance documents have been written and rewritten concerning the sampling of ground water for water quality assessment and monitoring purposes over the last 10 years (U.S. EPA 1982; NCASI 1982; Claasen 1982; Gillham et al. 1983; Barcelona et al. 1985; U.S. EPA 1986; Blegen et al. 1987; Barcelona et al. 1987; EPRI 1985; Nielsen 1991; U.S. EPA 1991a; U.S. EPA 1991b). The inaccessibility and heterogeneity of the subsurface environment due to complex physical, chemical, geological, and biological processes have continuously required re-evaluation of sampling techniques and equipment as more is learned of the importance or significance of these processes with respect to subsurface contaminant fate and transport. It is widely acknowledged that "representative" (indicative of in situ water quality) ground water samples are at best difficult to obtain as a result of these complexities and constraints (Grisak et al. 1978; Gibb et al. 1981; Schuller et al. 1981; U.S. EPA 1982; Gillham et al. 1983; Barcelona et al. 1987; U.S. EPA 1991b). There has always been almost universal agreement that to obtain representative samples, subsurface disturbance and sample handling must be kept to a minimum to prevent sample alteration. However, disturbance of the subsurface in the course of sample acquisition is, to some extent, inevitable. The

argument then becomes the extent or significance of the disturbance and the magnitude of the induced physical and chemical changes. Intuitively, it makes sense that the approach that involves the least disturbance of the sampling point or change in the chemical properties of the sample is best.

The primary focus of ground water sampling issues over this same time period has been on organic contaminants. The loss of volatile organic constituents due to degassing and aeration during sample collection, handling, transport, and storage has been of particular concern. To minimize losses, careful control is recommended during sample transfer steps with respect to flow rate, atmospheric exposure, turbulence, and preservation (Barcelona et al. 1985). Degassing, depressurization, aeration, and turbulence can also adversely impact the collection of representative inorganic samples (Humenick et al. 1980; Gibb et al. 1981; NCASI 1982; Gillham et al. 1983; U.S. EPA 1986; EPRI 1987; Kent and Payne 1988). A significant difference (from the standpoint of ground water quality monitoring) between organic and inorganic contaminants is that organic contaminants are generally not naturally present in the subsurface, while inorganic contaminants are present in trace amounts as part of the geologic matrix. In an effort to differentiate between matrix elements and introduced inorganic contaminants, filtration of ground water samples is often recommended for metals. The term metal,

strictly speaking, applies only to those elements having characteristic metallic luster and high electric and thermal conductivity (e.g., Mg, Cd, Ni, Zn). However, metalloids or elements that have intermediate luster and conductivity (e.g., As, Se, Sb, Te) are also often included as metals and will be treated likewise in this paper.

Our position in this paper is that most current methods used to recover ground water quality samples for metals ignore some of the same constraints or limitations recognized for the collection of samples for other classes of contaminants, and in so doing, result in the collection of non-representative and non-reproducible samples for determination of ground water quality and risk assessment. The two primary factors affecting sample quality are excessive pumping rate (or water entrance velocity from the formation into the well and from the well into the sampling device) and filtration. To a large extent these two factors are interrelated, with the former often exacerbating the effects of the latter. We recommend the use of low flow rates, during both purging and sampling, placement of the sampling intake at the desired sampling point, minimal disturbance of the stagnant water column above the screened interval, monitoring of water quality indicators during purging, minimization of atmospheric contact with samples, and collection of unfiltered samples for metal analyses (Puls and Barcelona 1989; Puls et al. 1990; Puls et al. 1991). These recommendations and much of the following discussion assumes the use of portable sampling equipment (non-dedicated systems). In the majority of cases, these recommendations will result in low turbidity samples precluding the need for filtration, resulting in less sample handling and fewer sampling artifacts, and including the potentially mobile colloidal-associated metal contaminant fraction that would otherwise be eliminated.

Well Construction and Well Development

It is inevitable that monitoring well installations disrupt the formation to be sampled. The disruptions that occur can have significant impacts on the samples obtained from the well, potentially biasing results and causing the aqueous geochemistry of the formation at that point to be misrepresented. It is therefore necessary to minimize these impacts at every stage of the process, from drilling through installation and development. Well installation techniques and choice of appropriate well construction materials have been addressed in a number of publications (Scalf et al. 1981; Gillham et al. 1983; Barcelona et al. 1985; Barcelona et al. 1987; U.S. EPA 1991b; Marsh and Lloyd 1980; Barcelona and Helfrich 1986). Of particular importance in fine-grained sediments is the appropriate selection of filter pack materials and well screen slot size.

Well development should be performed as soon as possible following well construction. Well development is necessary to remove the loose particulates present in the well from the construction activities and to unblock the layers adjacent to the well screen that may have been smeared by clays or had their surface structures broken down and obstructed during drilling, thus limit-

ing ground water flow. Several common methods of well development, along with their advantages and disadvantages, are described in Scalf et al. (1981), Keeley and Boateng (1987), and Barcelona et al. (1987). Methods that force water or air into the formation should be avoided. For example, air jetting could cause changes in the redox conditions of the formation zone around the screen and possibly result in trapped air pockets that could restrict water flow and exert longer term effects on water chemistry. Excessively disruptive turbulence during any of these techniques could damage the sand pack, resulting in channeling of waters that might bias sample chemistry. Probably the most widely accepted development technique is simply to pump the well using a pump intake that is raised and lowered (without excessive surging) throughout the length of the screened interval. The optimum pumping rate will vary with well-specific factors, such as hydrologic environment, screen length, casing diameter, etc., and no generally applicable guidelines can be provided at this time. Turbidity during development will initially be quite high. As the water becomes clear it would be useful to measure turbidity over time to determine when a stable value has been achieved and development can be discontinued. Many references state that the goal of monitoring well construction in general, and well development specifically, is to obtain turbidity-free samples. It is true that artificially induced turbidity is undesirable, but it must also be realized that naturally occurring or contaminant-induced particulates might be mobile in aquifers under certain conditions and capable of transporting sorbed contaminants. When these particles are naturally present, neither the development water nor subsequent samples taken from the well will necessarily achieve a turbidity-free condition.

Samples should not be taken immediately following well development. A sufficient time should elapse to allow the ground water flow regime in the vicinity of the monitoring well to stabilize and to let chemical equilibrium with the well construction materials be approached. This lag time will depend on site- and installation-specific parameters.

Well Purging

It is generally agreed that the purging of monitoring wells for the purpose of obtaining representative samples is necessary in most instances (U.S. EPA 1982; NCASI 1982; Claassen 1982; Gillham et al. 1983; Barcelona et al. 1985; EPRI 1987; Nielsen 1991; U.S. EPA 1991b). Ground water chemistry can be altered through contact with well casing, screen, filter pack, and annular seal materials (U.S. EPA 1982; Barcelona et al. 1985; Barcelona and Helfrich 1986). Controversies surrounding well purging concern the manner in which the well is purged and the required duration (Marsh and Lloyd 1980; Gillham et al. 1983; Giddings 1983; Keeley and Boateng 1987; Gibbs and Imbrigiotta 1990). As previously indicated, the goal is the acquisition of a water sample from the geologic material being sampled with the least disturbance (U.S. EPA 1991b). Some researchers have indicated less need for purging in wells in which

dedicated sampling equipment is installed, or where disturbance of the stagnant water column above the screened interval is minimized during sample acquisition (Pickens et al. 1978; Robin and Gillham 1987). Several sampling guidance documents and investigators have suggested a standard number of well casing volumes (NCASI 1982; U.S. EPA 1986; Feld et al. 1987; U.S. EPA 1991a), but others point to potential drawbacks of this approach, including the practice being too time-consuming and costly, the generation of unnecessarily large volumes of contaminated water for disposal, mixing of chemically distinct waters, and excessive disturbance of the well at the sampling point leading to artificially induced chemical changes (Gillham et al. 1983; Giddings 1983). Schuller et al. (1981) and, later, Barcelona et al. (1985) proposed the establishment of purging strategies based on the following:

1. well hydraulic performance
2. calculation of reasonable purge requirements, pumping rates, and volumes based on hydraulic conductivity data, well construction data, site hydrologic conditions, and anticipated water quality
3. measuring the well purging parameters to verify "equilibrated" conditions.

Several investigators have suggested monitoring certain water quality indicators during purging to provide an indication of equilibrated and hopefully representative conditions at the sampling point (Claasen 1980; Gibb et al. 1981; Giddings 1983). While most references refer only to temperature, specific conductance, and pH as the appropriate indicators, some include redox, dissolved oxygen, and contaminant concentrations. Pionke and Urban (1987) found temperature, specific conductance, and pH to equilibrate in less than one casing volume in most wells studied, with dissolved oxygen and nitrate concentrations requiring longer intervals (pump-

ing rates of 10.6 to 17.4 L/min). Results from work done by Humenick et al. (1980) showed specific conductance to be relatively insensitive as an indicator parameter, where temperature, pH, redox, and alkalinity were also monitored. Using flow rates of 15.1 to 22.7 L/min, they observed equilibration of indicator parameters in less than one well volume for most wells sampled. Gibb and Imbrigiotta (1990), using pumping rates of 3.8 to 97.3 L/min, found that most indicators equilibrated in less than three casing volumes, but purgeable organics equilibrated within three casing volumes in only 55 percent of the cases evaluated. This was particularly evident in most of the high pumping rate cases. Puls et al. (1991 and 1992) have shown temperature, specific conductance, and pH to be the least sensitive indicators of aquifer re-equilibration, while redox, dissolved oxygen, and contaminant concentrations are more sensitive and turbidity is the most sensitive indicator of equilibrated conditions (Figure 1). The recent development of inline flow-through cells capable of continuously monitoring most of these constituents and reliable field kits for other parameters make these determinations more practical and more widely available than in the past.

Pumping Rate

The latter studies (Puls et al. 1991 and 1992) used very low pumping rates (0.2 to 3.8 L/min) during purging, while many of the previous recommendations have been based on rates well in excess of this range. The pumping rate used during purging has been shown to affect many of these indicators (Pionke and Urban 1987; Puls et al. 1991; NCASI 1982). Results suggest that the order of sensitivity and time for re-equilibration is directly related to purging rate, location of the pump inlet, and extent of disturbance of the overlying stagnant water column in the well. It is interesting to note that

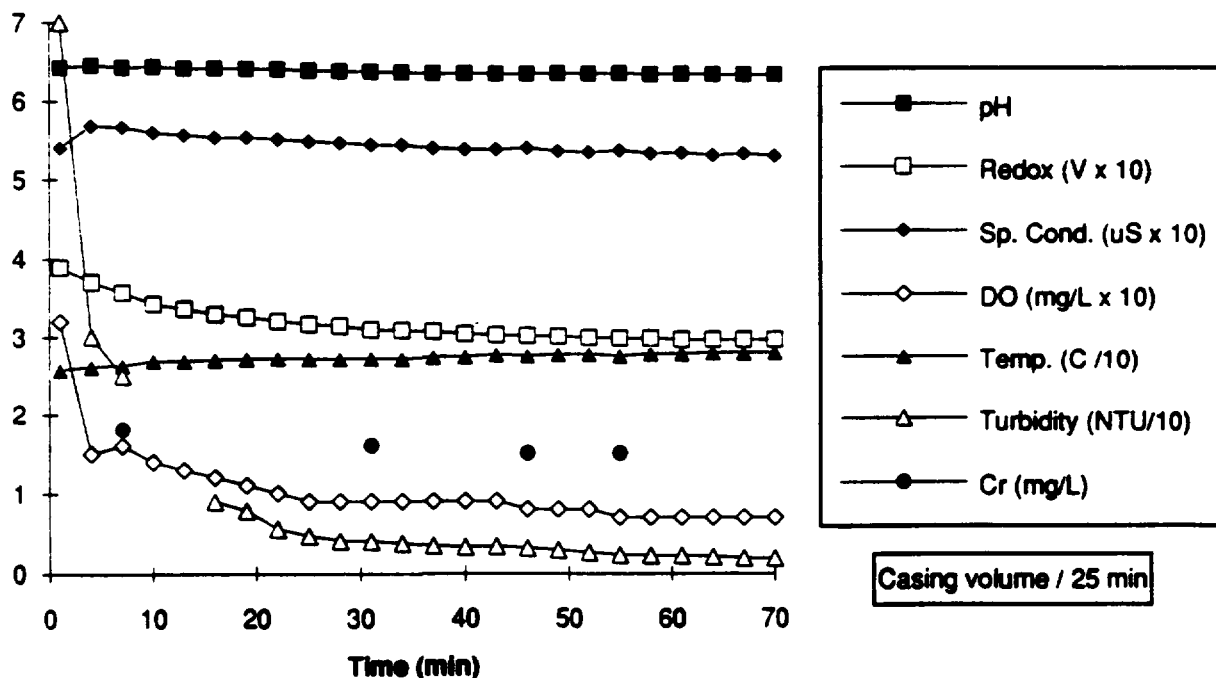


Figure 1. Equilibration of ground water quality indicators during purging and sampling (well 17, Elizabeth City, North Carolina; Grundfos Redi-Flo2 submersible pump, 0.2 L/min).

in the three distinctly different sites studied to date by Puls et al. (1991 and 1992), equilibration of pH, specific conductance, and temperature consistently occur in less than one casing volume and even the most sensitive indicator (turbidity) generally stabilizes in less than three casing volumes under low flow rate conditions. Barcelona et al. (1985) suggest that purging with such low flow rates (with the pump intake just above or within the screened interval) in effect isolates the stagnant column of water in the well bore and negates the need for its removal. This is consistent with the observations of Robin and Gillham (1987), who found that in many formations the water within the screened interval is representative of the formation water and chemically distinct from the overlying stagnant water column. Keeley and Boateng (1987) concur, but caution against the use of bailers following "passive" purging, whereby the bailer passes through the stagnant zone causing mixing, thus negating the benefits of the low flow rate purge.

The effects of pumping rate (or the entrance velocity of water from the formation into the well and subsequently into the sampling intake) of particular concern are turbulence, redevelopment of the well, mixing of chemically distinct zones, and aeration. These effects can induce physical and chemical changes which include excessive turbidity; exposure of fresh sorptive surfaces in suspension capable of adsorbing dissolved metals; dilution or concentration of contaminants due to mixing; changes in pH, carbonate equilibria, metal speciation, and redox; and chemical precipitation. While most investigators and ground water sampling guidance documents acknowledge these effects and their potential for adverse impact on water quality samples, only a few go so far as to recommend using very low flow rate pumping to minimize them (Barcelona et al. 1985; U.S. EPA 1986; Feld et al. 1987; Puls and Barcelona 1989), and most of these focus on impacts to volatile organic constituents rather than metals.

The development of turbulent flow at the sampling point invariably results in excessive turbidity which may or may not decline during purging and sampling. This is exacerbated in fine-textured zones and with the use of high-speed pumps and bailers. Problems using bailers are often associated with operator technique. When a bailer is used to purge wells, the continual raising and lowering can act like a plunger in the wellbore and, in worst cases, result in continual development and/or overdevelopment of the well. Most bailers fill rapidly and entrance velocities can exceed even those of high-speed pumps. If used strictly as a sampling device, there is often uncertainty as to the zone actually being sampled. When passed through the stagnant water column above the screen (without proper purging), the resulting mixing will produce a non-representative sample.

A downhole camera was recently used by Robert S. Kerr Environmental Research Laboratory (RSKERL) personnel in cooperation with researchers from Oak Ridge National Laboratory to observe the impacts of sampling device insertion and pumping rate in a number of wells at two different sites. It was observed that much

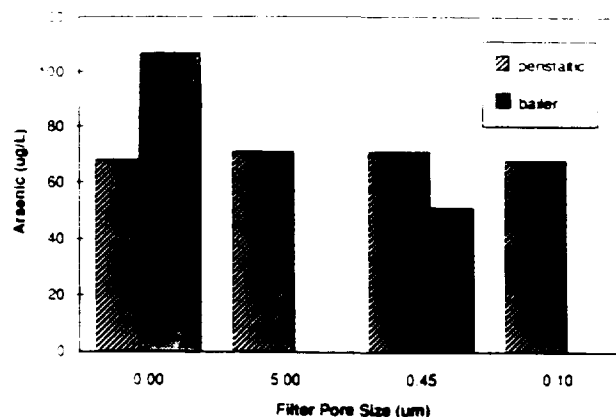


Figure 2a. Differences in arsenic concentrations for samples collected with peristaltic pump (0.2 L/min) and dedicated bailer (well 101, Saco, Maine).

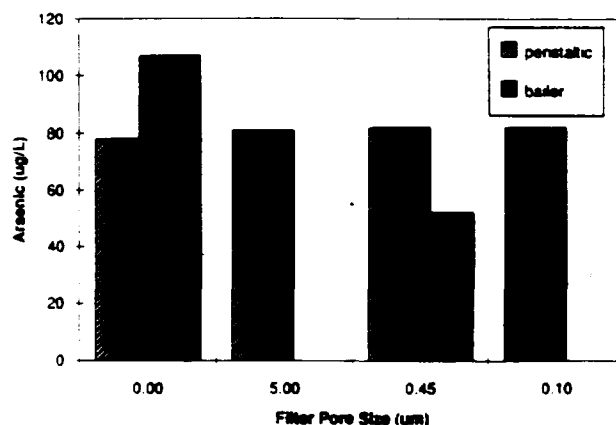


Figure 2b. Differences in arsenic concentrations for samples collected with peristaltic pump (0.2 L/min) and dedicated bailer (well 114b, Saco, Maine).

of the disturbance (measured as turbidity) was due to the initial sampling device emplacement. Colloidal density (quantitatively measured with a turbidimeter and qualitatively by visual observation) was observed to decline exponentially while purging at low flow rates. Without purging, the initial disturbance (turbidity) required overnight equilibration to attain comparable low turbidity values and stable flow in the screened interval. In some cases, considerable turbidity may represent the natural flow condition in that part of the aquifer in which the wells are screened. This can be due to the following: fine-grained sediments, high natural flow rates, aqueous chemistry promoting colloid stability, and geochemical transients due to waste disposal (e.g., pH and redox changes). A number of field studies (Ryan and Gschwend 1990; Buddemeier and Hunt 1988) have indicated elevated levels of "natural" turbidity where suspended particle concentrations could significantly impact the mobility of contaminants. Samples displaying high turbidity, however, are generally due to poor well development (Paul et al. 1988) or sampling artifacts (Puls et al. 1991) and the result is typically large discrepancies between field-filtered and unfiltered metal samples.

Figures 2a-b display data from a Superfund site, where arsenic is a contaminant of interest. Differences

TABLE 1
Arsenic Concentrations and Turbidity
Obtained by a Contractor (Bottom-Filling
Bailer, Quarterly Sampling) from Selected
Wells at a Superfund Site,
July and November, 1990

Well	Arsenic ($\mu\text{g/L}$)			Turbidity (NTU)
	July 1990 0.45 μm Filtered	July 1990 Unfiltered	Nov. 1990 0.45 μm Filtered	Nov. 1990
101	51	107	67	97
103	85	177	64	96
111b	24	223	48	>200
112a	40	85	124	5
114b	52	107	52	81

in arsenic concentrations were negligible using a peristaltic pump and when samples were collected after all water quality parameters had equilibrated and turbidity was less than 10 nephelometric turbidity units (NTUs). In contrast, a low-turbidity sample could not be obtained for the bailed samples where the bailer was used both to purge and sample the wells. Dedicated Teflon® bailers were routinely used at the site to purge and sample all wells quarterly. Table 1 lists data for two different quarterly monitoring results for this site, where most of the wells are screened in fine-grained glacial till. In July of 1990, both unfiltered and field-filtered samples were collected by the contractor, whereas in November, only filtered samples were collected. Turbidity data are available from the contractor only for the latter sampling event. Obvious differences between filtered and unfiltered arsenic concentrations exist in the data set. Unfiltered arsenic values are 2.1 to 9.7 times the filtered values. In the November data, elevated turbidity levels were present in all the samples except those from well 112A, where the significantly lower turbidity value occurs in the only sample in which the arsenic value is higher than the unfiltered data.

TABLE 2
Arsenic Concentrations and Turbidity
Obtained by R.S. Kerr Environmental
Research Laboratory Personnel (Peristaltic
Pump, 0.2 L/min) from Superfund Site,
July 1990

Well	Arsenic ($\mu\text{g/L}$)				Turbidity (NTU)
	0.1 μm	0.45 μm	5.0 μm	Unfiltered	
101	68	71	71	68	9.5
103	202	230	232	241	4.0

The authors sampled some of these same wells a week after the contractor, in July 1990, using low flow rate purging and sampling as previously described. Filtration was accomplished with high-capacity in-line filters. No significant differences were observed in arsenic concentrations whether the samples were filtered or not

Table 2. Interestingly, the 0.45 μm filtered samples collected by the contractor with the bailer had consistently lower arsenic concentrations than the low flow rate pumped samples obtained with the peristaltic pump. Differences may have been due to filter clogging from excessive fines, reducing the effective pore size of the filters, or adsorption onto freshly exposed surfaces brought into suspension artificially. Similar results were observed in all wells sampled in this manner, and as a result this sampling approach was adopted for subsequent routine monitoring. Another Superfund site, located in the same geologic region, has also adopted this sampling approach, again with extremely consistent results (i.e., excellent reproducibility and no differences between field-filtered and unfiltered data). Using low flow rate purging and sampling techniques for metals at three sites, we have repeatedly demonstrated no significant differences between filtered and unfiltered metal samples. Details of the approach are found in Puls and Barcelona (1989) and Puls et al. (1991), but essentially the approach entails low flow rate purging and sampling (0.2 to 0.3 L/min), in-line monitoring of pH, temperature, specific conductance, redox, dissolved oxygen, and turbidity, and collection and immediate processing of samples upon indicator equilibration.

While turbidity is the most obvious impact of bailing or excessive pumping, the effect of metal adsorption onto previously immobile and perhaps unexposed surfaces or onto previously non-precipitated solids are other explanations for contaminant concentration differences. From an operational definition standpoint, the unfiltered fraction should represent "total" metal concentrations which include dissolved, adsorbed, coprecipitated, and matrix (or non-surface associated metal fractions). The filtered fraction should represent "dissolved" or the non-particulate associated fraction. The distribution of metals between the solid and liquid fractions is generally in equilibrium in the target sampling environment. However, this distribution may be artificially altered by excessive sampling zone disturbance caused by bailing or excessive pumping, with the introduction of freshly exposed reactive surfaces through precipitation, particle detachment, or disaggregation. Iron oxyhydroxide precipitation from a neutral solution in contact with the atmosphere ($P_{O_2} = 0.2 \text{ atm}$) containing 1 mM Fe^{2+} can occur within minutes (Grundl and Delwiche 1992). This ubiquitous solid phase possesses extremely high reactivity (capacity and rapid kinetics) for many metal species. Typical sample collection practices with bailers (including a filtration step) require significantly more time. Most metal adsorption reaction rates are extremely rapid (Sawhney 1966; Posselt et al. 1968; Forbes et al. 1976; Benjamin and Leckie 1981; Sparks et al. 1980; Aringhieri et al. 1985). Anderson et al. (1973) reported up to 95 percent adsorption of arsenic onto amorphous aluminum hydroxide within the initial few minutes of their experiments. Researchers are often constrained in adsorption kinetic experiments because the reactions occur faster than they are capable of detecting even under controlled laboratory conditions (Ferguson and Anderson 1973; Puls 1986; Barrow et al.

1987). In addition, reduced adsorption rates are generally observed with increased shaking or stirring, because diffusion is most often the rate-limiting step (Mortland and Ellis 1959). Salm and Cooksey (1980) demonstrated that the adsorption of lead onto sediments was primarily diffusion rate-limited, and increased with agitation of the suspension and increasing temperature. They observed more than three times as much adsorption in samples that were agitated (stirred) than in those that were not. Therefore, the assumption that the separation of suspended particulates from water samples to be analyzed eliminates only matrix metals may often be incorrect (EPRI 1985; Feld et al. 1987). This non-conservative artifact, which is caused by poor sampling techniques (i.e., bailing, excessive pumping), is magnified depending upon several factors in addition to pumping rate, which include the following: kinetics of the adsorption reaction (varies with the metal), depth of the sampling point, aqueous chemistry, and sample processing procedures at the surface.

Spatial variability in aquifer water chemistry has been observed by several investigators (Back 1966; Veatch 1969; Payne 1975). Other studies have demonstrated the existence of complex and variable contaminant plumes (Schmidt 1977; Schmidt 1982; Keeley 1982; Keeley and Wolf 1983). To deal with the variability of contaminant concentration distributions and aquifer heterogeneities and their potential impacts on the acquisition of accurate water quality samples, Humenick et al. (1980) and Puls and Barcelona (1989) have recommended the use of low flow rate purging and sampling. These techniques avoid mixing of distinctly different geochemical waters and the smearing of contaminant distribution resolution. Recently, Ronen et al. (1987) and Hoffman and Dresen (1990) have tested and recommended the use of an in situ multilevel sampler and a wireline punch-coring system, respectively, to improve resolution of contaminant distribution in aquifers. Similar devices have also been recently developed and mar-

keted commercially. When used as indicated, such low flow rate pumping provides us with gross average contaminant concentrations and inaccurate plume delineation; more emphasis should be placed on the development of "passive" sampling techniques.

Filtration

As indicated, filtration is often recommended to separate formation matrix metals from dissolved contaminants (Standard Methods for the Examination of Water and Wastewater 1989, Method 3030; U.S. EPA 1979). This separation is purely artificial with the 0.4 or 0.45 μm pore size as the operationally defined separation between particulate (solid) and dissolved. In contrast, the definition provided by the ASTM Committee on Water (D-19) specifies dissolved more correctly as "that matter, exclusive of gases, which is dispersed in water to give a single homogeneous liquid phase." Further, in ASTM Designation D-3370, they recommend collection of water samples from wells without separation of particulate matter and indeed specify the inclusion of colloidal constituents in representative proportions. Some investigators have suggested the collection of both field-filtered and unfiltered samples (U.S. EPA 1986; Nacht 1983; Puls and Barcelona 1989) for the purpose of risk assessment, with the latter authors specifying the importance of potentially mobile colloids in facilitating the transport of contaminants.

Aside from concerns or questions of colloid-associated transport, the potential for filtration-generated artifacts has been widely recognized and documented. These include filter clogging (Laxen and Chandler 1982), variable particle size retention characteristics (Sheldon 1965; Sheldon and Sutcliffe 1969), filter media leaching (Jay 1985), and aeration leading to precipitation (NCASI 1982; EPRI 1987). The latter effect can be particularly significant in suboxic and anoxic environments in which elevated levels of ferrous iron are typically present. The precipitation of ferric hydroxide

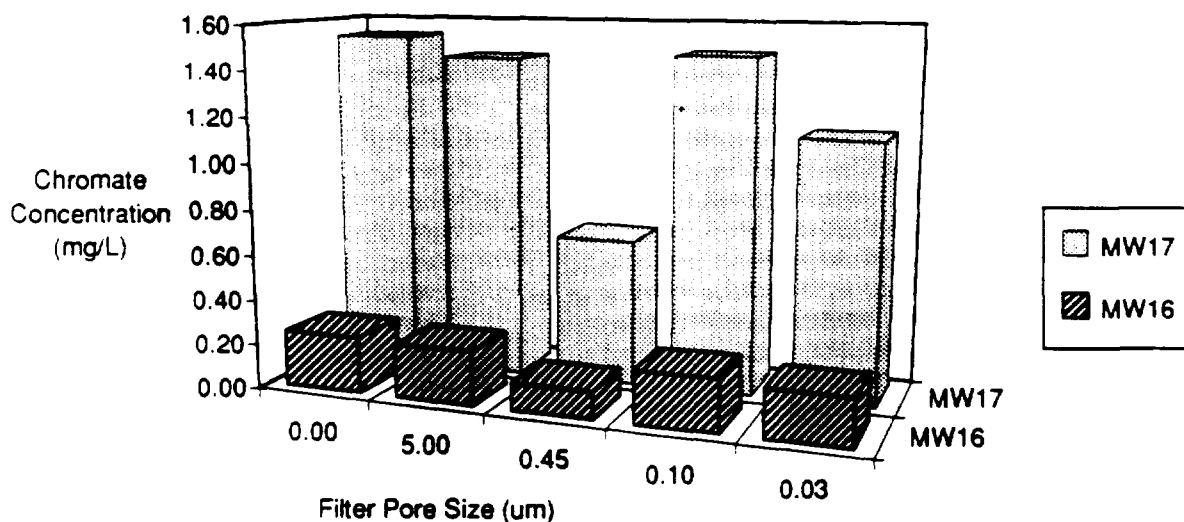


Figure 3. Differences in chromate concentrations using different filter pore sizes (0.00 = unfiltered) and filter type (0.45 μm , disposable high-capacity in-line; others, thin membrane polycarbonate [142 mm dia]) at two different wells at Elizabeth City, North Carolina (Grundfos Redi-Flo2 submersible pump, 0.2 L/min).

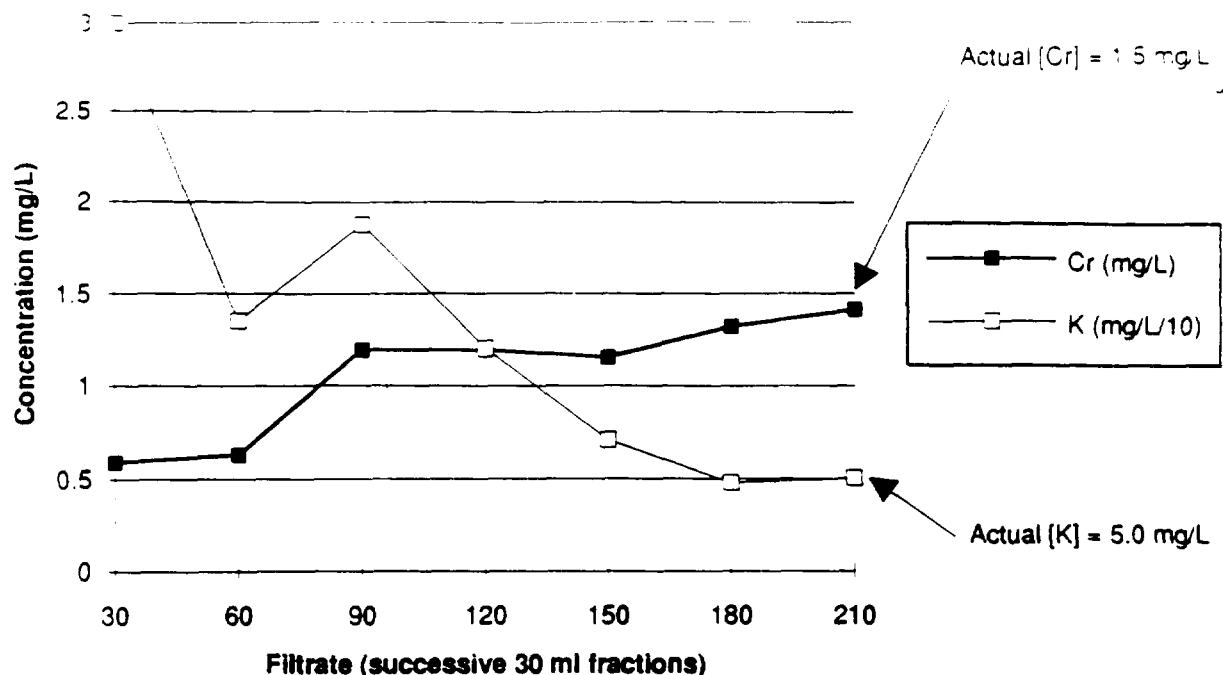


Figure 4. Effect of successive (30 mL aliquot) flushing on potassium and chromium concentrations through a disposable high capacity in-line filter.

can result in loss of dissolved metals due to rapid adsorption or coprecipitation, particularly affecting arsenic, cadmium, copper, lead, nickel, and zinc (Stolzenberg and Nichols 1985; Kent and Payne 1988; Kinniburgh et al. 1976). While aeration can be minimized with proper tubing considerations and in-line filtration, the other problems are still evident. Figure 3 illustrates discrepancies between samples collected using different filter types. Samples were collected using low flow rate (0.2 L/min) purging and sampling techniques from two wells at Elizabeth City, North Carolina. Both wells are completed at 15 feet below ground surface with 5-foot screens (0.010-inch slot size), and ground water is 7 feet below ground surface. The 0.45 μm filtered samples were obtained with high-capacity in-line disposable filters and the others with thin (142mm diameter) membrane polycarbonate filters (using an in-line holder). Significant differences (lower concentrations) were observed with the high-capacity filters. This was further investigated in the laboratory using the same ground water collected from the field site (Figure 4). With successive 30 mL filtrate sample collection, increasing concentrations of chromium and decreasing concentrations of potassium were observed in the filtrates, similar to the lower levels observed in the field samples for chromium, and elevated levels of potassium. Adsorption of chromium onto the filter media and leaching of potassium from the filter media were responsible for the observed discrepancies. While manufacturer recommendations indicated only a 200 mL rinse, this has subsequently been changed, as has the filter material. This demonstrates the importance of following and verifying manufacturer rinsing recommendations and documentation of sampling procedures, but also indicates the potential for filter-related sampling artifacts.

Several investigators have demonstrated that the use

of 0.45 μm filters for assessment of truly dissolved metal concentrations is erroneous (Laxen and Chandler 1982; Wagemann and Brunskill 1975; Kennedy and Zellweger 1974; Gibb et al. 1981), yet it is surprising how much this purely operational separation for dissolved is applied in its strictest sense. Laxen and Harrison (1981) found the majority of Cu, Fe, and Pb to be associated with colloidal and particulate size fractions in river water. Likewise, Kim et al. (1984) found the majority of rare earth elemental concentrations to be associated with colloidal species passing a 0.45 μm filter in ground water samples. Kennedy and Zellweger (1974) provide a strong case for the use of 0.1 μm field filtration for better estimates of dissolved metal concentrations. Our own studies have shown their arguments to be valid and practical for use in field applications (Puls et al. 1991).

Summary

Consistent with most recommendations to minimize physical or chemical alteration of the sample during withdrawal, we propose the collection of ground water quality samples for metals using low flow rate purging and sampling at the required or objective sampling point within the well, monitoring of appropriate water quality indicators to signal sample collection, and no filtration. This would provide an assessment of both dissolved and mobile particulate-associated metals available for potential transport. If estimates of dissolved metal concentrations are desired (e.g., for geochemical modeling purposes), then use of in-line 0.1 μm filters with large surface areas, at the wellhead, is recommended. Caution must still be exercised with respect to leaching or sorption by the filter media. Where conditions are such that the acquisition of low-turbidity samples is not feasible (due to geologic constraints), and this can be adequately documented, then an alternative (e.g., use of a coarse

After this information, more detail may need to be considered. However, coarse filtration should still be used in conjunction with other parts of the sampling protocol stated previously and should not be used to compensate for poor well construction, development, or sampling procedures. Standard methods of preservation and storage should be employed. A significant level of effort has been invested in establishing uniform laboratory analytical methods, while comparatively little effort has been invested in the development of uniform sampling methodologies. This deficiency often results in the production of variable and almost meaningless results, and a significant waste of time and money. It is incumbent upon the ground water monitoring, research, and regulatory communities to rectify this situation. A consistent, scientifically defensible ground water sampling approach for metals should be adopted among the many different U.S. environmental programs and agencies entrusted with the protection of our water resources.

Final Note

The foregoing discussion assumes that the most accurate and representative sample is the primary goal of any sampling effort. If this is not the case — that is, if questions of expediency outweigh the above considerations — then less attention to the aforementioned concerns may be warranted. However, this would also apply as well to analytical procedures, because the accuracy and precision of our analyses are only as good as the samples that are provided.

Acknowledgments

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Disclaimer

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References

Aringhieri, R., P. Carrai, and G. Petruzzelli. 1985. Kinetics of Cu^{2+} and Cd^{2+} adsorption by an Italian soil. *Soil Science*, v. 139, no. 3, pp. 197-204.

ASTM. 1989. Annual Book of ASTM Standards. Section 11, *Water and Environmental Technology*, v. 11.01, pp. 5-7, 104-110, 180-183-243.

Anderson, M.A., J.P. Connelly, and D.E. Lindorff. 1987. Arsenate adsorption on amorphous aluminum hydroxide. *Journal of Colloid and Interface Science*, v. 54, no. 3, pp. 391-399.

Back, W. 1966. Hydrochemical Facies and Ground Water Flow Patterns in the Northern Part of the Atlantic Coastal Plain. U.S. Geological Survey Prof. Paper 498-A, 42 pp.

Barcelona, M.J., J.P. Gibb, J.A. Helfrich, and E.E. Garske. 1985. Practical Guide for Ground Water Sampling. EPA/600/2-85/104, 169 pp.

Barcelona, M.J., and J.A. Helfrich. 1986. Well construction and purging effects on ground water samples. *Environmental Science and Technology*, v. 20, no. 11, pp. 1179-1184.

Barcelona, M.J., J.F. Keeley, W.A. Pettyjohn, and A. Wehrmann. 1987. Handbook: Ground Water. EPA/626/6-87/016, 212 pp.

Barrow, N.J., J. Gerth, and G.W. Brunner. 1989. Reaction kinetics of the adsorption and desorption of nickel, zinc, and cadmium by goethite II modelling the extent and rate of reaction. *Journal of Soil Science*, v. 40, pp. 437-450.

Benjamin, M.M., and J.O. Leckie. 1981. Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. *Journal of Colloid and Interface Science*, v. 79, no. 1, pp. 209-221.

Buddemeir, R.W., and J.R. Hunt. 1984. Transport of colloidal contaminants in ground water: Radionuclide migration at the Nevada test site. *Applied Geochemistry*, 3:535-548.

Classen, H.C. 1982. Guidelines and Techniques for Obtaining Water Samples that Accurately Represent the Water Chemistry of an Aquifer. U.S. Geological Survey Open File Report 82-1024, 49 pp.

Clesceri, L.S., A.E. Greenberg, and R.R. Trussell, Eds. 1989. Standard methods for the examination of water and wastewater. *American Public Health Association*, pp. 3-7.

EPRI. 1985. *Field Measurement Methods for Hydrogeologic Investigations: A Critical Review of the Literature*. Electric Power Research Institute. EA 4301, 241 pp.

EPRI. 1987. *Sampling Guidelines for Ground Water Quality*. Electric Power Research Institute. EA-4952, 47 pp.

Feld, J., J.P. Connelly, and D.E. Lindorff. 1987. Ground water sampling — Addressing the turbulent inconsistencies. *Proceedings of the First National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring, and Geophysical Methods*, May 18-21. National Water Well Association, Dublin, Ohio, pp. 237-251.

Forbes, E.A., A.M. Posner, and J.P. Quirk. 1976. The specific adsorption of divalent Cd, Co, Cu, Pb, and Zn on goethite. *Journal of Soil Science*, v. 27, pp. 154-166.

Ferguson, J.F., and M.A. Anderson. 1973. Chemical forms of arsenic in water supplies and their removal. *Chemistry of Water Supply, Treatment, and Distribution*, Rubin, A.J., Ed. Ann Arbor Science Publ..

- Gibbs, J., and T.E. Imbrigiotta. 1990. Well-purging criteria for sampling purgeable organic compounds. *Ground Water*, v. 28, no. 1, pp. 68-78.
- Gibb, J.P., R.M. Schuller, and R.A. Griffin. 1981. Collection of representative water quality data from monitoring wells. Land disposal: Municipal solid waste. *Proceedings of the Seventh Annual Research Symposium at Philadelphia*, March 16-18, pp. 126-137.
- Giddings, T. 1983. Bore-volume purging to improve monitoring well performance: An often mandated myth. *Proceedings of the Third National Symposium on Aquifer Restoration and Ground Water Monitoring*, May 25-27, National Water Well Association, pp. 253-256.
- Gillham, R.W., M.J.L. Robin, J.F. Barker, and J.A. Cherry. 1983. American Petroleum Institute. API Publication 4367, 206 pp.
- Grisak, G.E., R.E. Jackson, and J.F. Pickens. 1978. Monitoring ground water quality: The technical difficulties. *Proceedings of the Establishment of Water Quality Monitoring Programs*, American Water Resources Association, pp. 210-232.
- Grundl, T., and J. Delwiche. 1992. Kinetics of Ferric Oxyhydroxide Precipitation. submitted *Geochimica et Cosmochimica Acta*.
- Hoffman, F., and M.D. Dresen. 1990. A method to evaluate the vertical distribution of VOCs in ground water in a single borehole. *Ground Water Monitoring Review*, pp. 95-100.
- Humenick, M.J., L. Jan Turk, and M.P. Colchin. 1980. Methodology for monitoring ground water at uranium solution mines. *Ground Water*, v. 18, no. 3, pp. 262-273.
- Jay, P.C. 1985. Anion contamination of environmental water samples introduced by filter media. *Analytical Chemistry*, v. 57, pp. 780-782.
- Keeley, J.F. 1982. Chemical time-series sampling. *Ground Water Monitoring Review*, v. 2, no. 4, pp. 29-38.
- Keeley, J.F., and F. Wolf. 1983. Field applications of chemical time-series sampling. *Ground Water Monitoring Review*, v. 3, no. 4, pp. 26-33.
- Keeley, J.F., and K. Boateng. 1987. Monitoring well installation, purging, and sampling techniques - Part I: Conceptualizations. *Ground Water*, v. 25, no. 3, pp. 300-313.
- Kennedy, V.C., and G.W. Zellweger. 1974. Filter pore-size effects on the analysis of Al, Fe, Mn, and Ti in water. *Water Resources Research*, v. 10, no. 4, pp. 785-789.
- Kent, R.T., and K.E. Payne. 1988. Sampling ground water monitoring wells: Special quality assurance and quality control considerations. In *Principals of Environmental Sampling*, American Chemical Society, pp. 231-246.
- Kim, J.I., G. Buckau, F. Baumgartner, H.C. Moon, and D. Lux. 1984. Colloid generation and the actinide migration in gorleben groundwaters. In *Scientific Basis for Nuclear Waste Management*, v. 7, Gary L. McVay, Ed., Elsevier, New York pp. 31-40.
- Kinniburgh, D.G., M.L. Jackson, and J.K. Syers. 1976. Adsorption of alkaline earth, transition, and heavy metal cations by hydrous gels of iron and aluminum. *Soil Science Society American Journal*, v. 40, pp. 796-799.
- Laxen, D.P.H., and I.M. Chandler. 1982. Comparison of filtration techniques for size distribution in freshwaters. *Analytical Chemistry*, v. 54, pp. 1350-1355.
- Laxen, D.P.H., and R.M. Harrison. 1981. The physiochemical speciation of Cd, Pb, Cu, Fe, and Mn in the final effluent of a sewage treatment works and its impact on speciation in the receiving river. *Water Research*, v. 15, pp. 1053-1065.
- Marsh, J.M., and J.W. Lloyd. 1980. Details of hydrochemical variations in flowing wells. *Ground Water*, v. 18, no. 4, pp. 366-373.
- Mortland, M.M., and B.G. Ellis. 1959. Release of fixed potassium as a diffusion-controlled process. *Soil Science Society America Proceedings*, v. 23, pp. 363.
- Nacht, S.J. 1983. Monitoring sampling protocol considerations. *Ground Water Monitoring Review*, v. 3, no. 3, pp. 23-29.
- Nielsen, D.M. (ed) 1991. *Practical Handbook of Ground Water Monitoring*, Lewis Publishers, Chelsea, Michigan, 717 pp.
- NCASI. 1982. A Guide to Ground Water Sampling. National Council of the Paper Industry for Air and Stream Improvement. Tech. Bull. No. 362, 53 pp.
- Paul, D.G., C.D. Palmer, and D.S. Cherkauer. 1988. The effect of construction, installation, and development on the turbidity of water in monitoring wells in fine-grained glacial till. *Ground Water Monitoring Review*, v. 8, no. 1, pp. 73-82.
- Payne, J.N. 1975. Geohydrologic Significance of Lithofacies of the Carrizo Sand of Arkansas, Louisiana, Texas, and the Meridian Sand of Mississippi. U.S. Geol. Survey Prof. Paper 569-D, 11 pp.
- Pickens, J.F., J.A. Cherry, G.E. Grisak, W.F. Merritt, and B.A. Risto. 1978. A multilevel device for ground water and piezometric monitoring. *Ground Water*, v. 16, no. 5, pp. 322-327.
- Pionke, H.B., and J.B. Urban. 1987. Sampling the chemistry of shallow aquifer systems - A case study. *Ground Water Monitoring Review*, v. 7, no. 2, pp. 79-88.
- Posselt, H.S., F.J. Anderson, and W.J. Weber Jr. 1968. Cation sorption on colloidal hydrous manganese dioxide. *Environmental Science and Technology*, v. 2, p. 1087.
- Puls, R.W. 1986. Adsorption of Heavy Metals on Soil Clays. Ph.D. Dissertation, University of Arizona, 144 pp.
- Puls, R.W., and M.J. Barcelona. 1989. Filtration of ground water samples for metals analysis. *Hazardous Waste and Hazardous Materials*, v. 6, no. 4, pp. 385-393.
- Puls, R.W., J.H. Eycaner, and R.M. Powell. 1990. Colloidal-Facilitated Transport of Inorganic Contaminants in Ground Water: Part I. Sampling Considerations. EPA/600/M-90/023, 12 pp.
- Puls, R.W., R.M. Powell, D.A. Clark, and C.J. Paul. 1991. Facilitated Transport of Inorganic Contami-

- facts in Air and Water. Part II: Colloidal Transport. EPA 600/M-91-40. 12 pp.
- Puls, R.W., D.A. Clark, B. Bledsoe, R.M. Powell, and C.J. Paul. In press. Metals in ground water: Sampling artifacts and reproducibility. *Hazardous Waste and Hazardous Materials*.
- Robin, M.J.L., and R.W. Gillham. 1987. Field evaluation of well purging procedures. *Ground Water Monitoring Review*, v. 7, no. 4, pp. 85-93.
- Ronen, D., M. Margantz, and I. Levy. 1987. An in situ multilevel sampler for preventive monitoring and study of hydrochemical profiles in aquifers. *Ground Water Monitoring Review*, v. 7, no. 4, pp. 69-74.
- Ryan, J.N., and P.M. Gschwend. 1990. Colloid mobilization in two Atlantic Coastal Plain aquifers. *Water Resources Research*, v. 26, pp. 307-322.
- Salim, R., and B.G. Cooksey. 1980. Kinetics of the adsorption of lead on river-mud. *Plant and Soil*, v. 54, pp. 399-417.
- Sawhney, B.L. 1966. Kinetics of cesium sorption by clay minerals. *Soil Science Society of America Proceedings*, v. 30, p. 565.
- Scalf, M.R., J.F. McNabb, W.J. Dunlap, R.L. Cosby, and J.L. Fryberger. 1981. *Manual of Ground-Water Quality Sampling Procedures*. National Water Well Association. Dublin, Ohio, 93 pp.
- Schmidt, K.D. 1977. Water quality variations for pumping wells. *Ground Water*, v. 15, no. 2, pp. 130-137.
- Schmidt, K.D. 1982. How representative are water samples from wells? *Proceedings of the Second National Symposium on Aquifer Restoration and Ground Water Monitoring*. National Water Well Association. Dublin, Ohio, pp. 117-128.
- Schuller, R.M., J.P. Gibb, and R.A. Griffin. 1981. Recommended sampling procedures for monitoring wells. *Ground Water Monitoring Review*, v. 1, no. 2, pp. 42-44.
- Sheldon, R.W. 1965. Size separation of marine seston by membrane and glass-fiber filters. *Limnology and Oceanography*, v. 17, pp. 494-498.
- Sheldon, R.W., and W.H. Sutcliffe Jr. 1969. Retention of marine particles by screens and filters. *Limnology and Oceanography*, v. 14, pp. 441-444.
- Sparks, D.L., L.W. Zelazny, and D.C. Martens. 1980. Kinetics of potassium exchange in a paleudult from the Coastal Plain of Virginia. *Soil Science Society of America Journal*, v. 44, no. 1, pp. 37-40.
- Stolzenburg, T.R., and D.G. Nichols. 1985. Preliminary Results on Chemical Changes in Ground Water Samples Due to Sampling Devices. EPRI EA-4118, 53 pp.
- U.S. EPA. 1979. Methods for Chemical Analysis of Water and Wastes. EPA/600/4-49/020.
- U.S. EPA. 1982. Handbook for Sampling and Sample Preservation of Water and Wastes. EPA 600/4-82/029, 402 pp.
- U.S. EPA. 1986. RCRA Ground-Water Monitoring Technical Enforcement Guidance Document. OSWER 9950.1, 207 pp.
- U.S. EPA. 1991a. Compendium of ERT Ground Water Sampling Procedures. EPA/540/P-91/007.63 pp.
- U.S. EPA. 1991b. Handbook: Ground Water Volume II: Methodology. EPA/625/6-90/016b. 141 pp.
- Veatch, M.D. 1969. Ground Water Occurrence, Movement, and Hydrochemistry within a Complex Stratigraphic Framework. Jefferson County, Nebraska. Stanford Univ. Ph.D. Dissertation.
- Wagemann, R., and G.J. Brunskill. 1975. The effect of filter pore-size on analytical concentrations of some trace elements in filtrates of natural water. *International Journal of Environmental Analytical Chemistry*, v. 4, pp. 75-84.

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